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ANALYTICAL TECHNIQUES USING X-RAY FLUORESCENCE SPECTROMETRY

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16. Abstract

A description and some examples are given of how X-ray fluorescence spectrometry can be used in practical analysis of interest to the oil industry.

Details are submitted on qualitative analysis; quantitative analysis by the internal standard method; and on indirect quantitative analysis.

Virtually all elements can be analyzed with one of these methods, even if not all are as speedy and handy to use.

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ANALYTICAL TECHNIQUES USING X-RAY FLUORESCENCE SPECTROMETRY*

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/299**

INTRODUCTION

At the present state of the art of instrumentation, X-ray fluorescence spectrometry affords a direct analysis of elements with atomic weight higher than magnesium; accurate and precise determinations are obtained.

The sample, excited by the primary radiation of a Roentgen tube, emits radiations; these, after diffraction by a crystalline diffraction grating (LiF, polyethylene), give a fairly simple spectrum which is characteristic for each element.

Figure 1 shows an example of qualitative analysis: the Mo, Pb and Cu characteristic lines are present in the spectrum.

An accurate inspection of a qualitative spectrum requires approximately 40 minutes, but a confirmation of the presence or absence of specific elements can be carried out in a few minutes. /300

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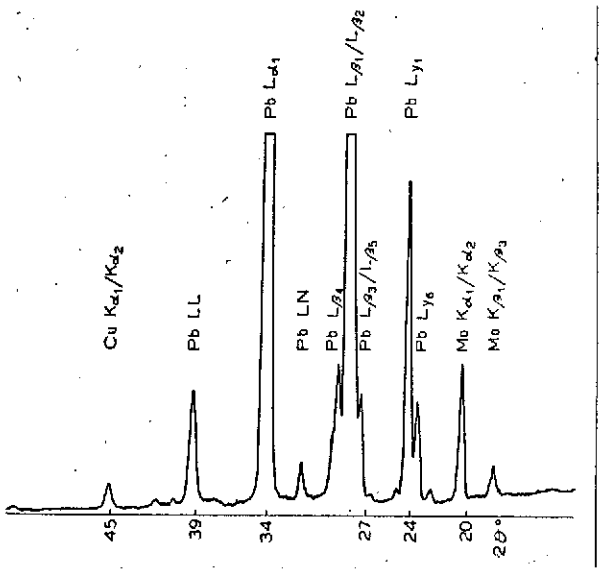

Figure 1._ Example of qualitative analysis of metals present in lubricating oil.

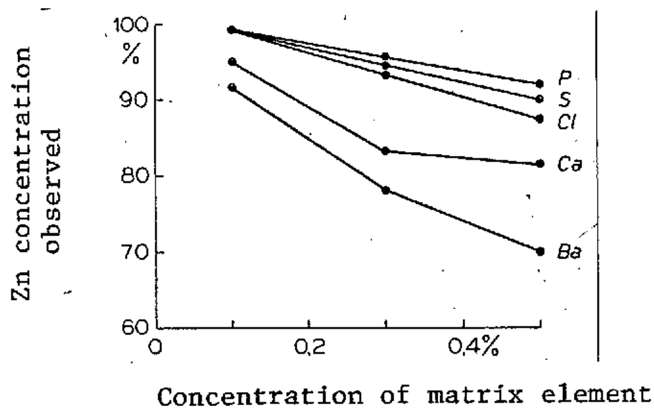

Figure 2. Matrix effect of various elements on the determination of zinc.

The most disparate samples (oils, aqueous solutions, greases, sediments, deposits, metallic samples) can be analyzed qualitatively by this technique in a fast and convenient way.

The intensity of fluorescent radiation, measured by an argon-methane flow meter or by a scintillation counter, can provide quantitative determinations of the concentration of an element. In most cases, this cannot be carried out by a simple direct measurement of the intensity of the fluorescent radiation, because, almost always, matrix effects due to the presence of other elements in the sample have to be taken into consideration.

Figure 2 shows the matrix effect of various elements (P, S, Cl, Ca, Ba) on the determination of zinc. It is evident that, if more elements were present in the sample, the concentration values observed for Zn could fall to 50% or less.

The most effective and accurate procedure for counteracting matrix effects is the use of an internal standard.

The element chosen as an internal standard has to supply a fluorescent radiation whose matrix effects are analogous to those of the radiation analyzed. The radiation of the internal standard is then used as a reference.

When choosing a suitable internal standard, the practical rule to consider for a first orientation is the following:
(i) no absorption thresholds of matrix elements can fall between the two analysis and reference fluorescence lines;
(ii) no fluorescence lines of interfering matrix elements fall between the absorption thresholds of the elements to be measured. However, only actual experiments can determine in practice if an element is suitable as internal standard.

In the case of Zn, for example, copper is usually selected as internal standard element.

The literature provides many examples of this procedure. Some laboratories use the internal standard technique to analyze simultaneously many elements in the same analytical sample. The simultaneous determination of five elements in the same analytical sample is considered the limit; this shows the convenience and speed of this procedure.

DETERMINATION OF ELEMENTS IN MINERAL OIL

The tables which follow illustrate a procedure for the determination of Ca, Ba, P, S, and Zn in oils.

Table 1 lists the internal standards used, the range of determination of the respective elements analyzed (P and S use Zn as common internal standard) and the two formulations for the analytical sample. Formulation I is used when all five elements are determined; formulation II — when only one element is determined, or when the concentration of the elements to be analyzed is below normal levels or approaches the lower limit. The two formulations are equivalent to each other, that is, the same calibration curve is used for both. /301

Table II summarizes the operating conditions for the spectrophotometer.

TABLE I. INTERNAL STANDARDS

Copper naphthenate	0.4% Cu
Manganese naphthenate	0.2% Mn
Tin octanoate	0.5% Sn
Zirconium naphthenate	6.0% Zr

(TABLE I Continued on next page)

TABLE I INTERNAL STANDARDS (CONTINUED)**

Element	Normal determination range	Lower limit
Zn	0,30 ÷ 0,03% p.	10 ppm
Ba	1,00 ÷ 0,10% p.	10 ppm
Ca	1,00 ÷ 0,10% p.	10 ppm
P	0,30 ÷ 0,03% p.	0,01%
S	2,00 ÷ 0,10% p.	(*)

(*) Specific procedure (see below)
** Translator's note: Commas in numbers represent decimal points.

Formulation of the analytical sample:	I	II
Oil in the sample g	10	10
Equal parts mixture of the four internal standards, g	8	—
Internal standard, g	—	1
Diluting oil, g	4	—
Total	22	11

TABLE II. OPERATING CONDITIONS

Target	Ca
Power	50 kV, 28 mA
Optical Path	Helium
Discrimination	Automatic
Count	20s (100s for phosphorus)
Counter:	
Scintillation for Zn	
Argon-methane flow for Ba, Ca, P, S	
Wavelength Setting:	
160 μ	for Zn
480 μ	for Ba, Ca, P, S
Grating:	
LiF	for Zn
Polyethylene	for Ba, Ca, P, S

TABLE III. OPERATOR GUIDE *

Element	Line Å	2
Zn	K_α 1,435	41,74
Cu	K_α 1,542	44,96
Background		43,00
Ba	L_α 2,775	37,02
Mn	K_α 2,103	27,83
Background		39,50
Background		26,50
Ca	K_α 3,360	45,20
Sn	L_α 3,600	48,63
Background		47,00
P	K_α 6,155	89,50
Zr	L_α 6,074	87,95
Background		90,70
S	K_α 5,373	75,85
Zr	L_α 6,074	87,95
Background		90,70
Background		78,00

Set value 2 for maximum reading

* Translator's note: Commas in numbers represent decimal points

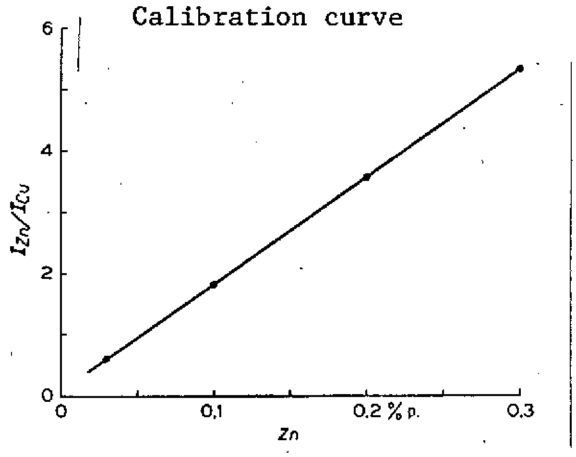

Figure 3. Example of calibration curve for X-ray analysis (zinc).

Table III is meant as a guide for the operator, who determines in succession the intensities of the various elements and the background value. The latter may be neglected if very low.

Figure 3 shows as an example the Zn calibration curve; other calibration curves (one for each element) are used in a similar way.

Table IV provides an indication of the accuracy of the procedure; the accuracy is the same or better than for chemical methods.

The time required for the analysis of four samples (preparation of the analytical formulation, readings, calculations, etc.) is approximately 2 hours with semi-automatic equipment and one operator; this may decrease to less than one hour with automatic equipment.

Table V provides other examples of analyses.

TABLE IV. ACCURACY * /302

Element	Level	Reproducibility (95% prob.)
Ba	0,10 ÷ 1,0	0,02
	0,02 ÷ 0,10	0,01
Ca	0,10 ÷ 1,00	0,03
	0,03 ÷ 0,10	0,01
Zn	0,03 ÷ 0,30	0,01
P	0,03 ÷ 0,30	0,015
S	0,1 ÷ 2,0	0,03

Accuracy is same as for chemical methods or better.

* Translator's note: Commas in numbers represent decimal points.

TABLE V. EXAMPLES OF ANALYSES *

Sulphur in oil products

Internal standard: Pb naphthenate (0,5 and 2,0% Pb)
Lines: S K_α 5,373 Å; Pb M_α 5,285 Å
Range: 0,001 ÷ 0,1 and 0,1 ÷ 2,0%
Internal standard: Zr octanoate (6% Zr)

Vanadium in residues and O.C.

Internal standard: Cr naphthenate (200 ppm Cr)
Lines: V K_α 2,505 Å; Cr K_α 2,290 Å
Range: 1 ÷ 300 ppm

Lead in oils

Internal standard: 0.5% Br (tetrabromoethane)
Lines: Pb L_α 0,982 Å; Br K_α 1,040 Å
Range: 0,1 ÷ 2,0%

* Translator's note: Commas in numbers represent decimal points

Among these, the procedure for the determination of sulfur utilizes, for the internal standard, lead naphthenate and the M Pb line. M series lines are not commonly used; it is useful to point out here that their use affords sulfur analyses with higher accuracy than with the ASTM D-2622 procedure. Sulfur analysis, for samples already containing lead (as in gasolines), is carried out using zirconium naphthenate as internal standard.

A suitable internal standard is not always available or in existence. In these cases, Tertian's simple dilution procedure can be used [1]. This technique overcomes matrix effects without the need of internal standards and calibration curves.

Four measurements are required: with the sample as is, with the sample diluted 1:1, with the reference sample, and with the reference sample diluted 1:1.

Tertian's formula to calculate the concentrations of the elements being analyzed is reported in Table VI.

TABLE VI. SIMPLE DILUTION PROCEDURE

$$\frac{CA}{CR} = \frac{(IA \cdot IAD)/(IA - IAD)}{(IR \cdot IRD)/(IR - IRD)}$$

CA = element concentration in the analysis sample.

CR = element concentration in the reference sample.

IA = line intensity of sample

IAD = line intensity of diluted sample

IR = line intensity of reference sample

IRD = line intensity of diluted reference sample

This procedure affords, for example, the determination of chlorine in oils in the 0.01-1.0% range, due to the fact that the potassium naphthenate internal standard is often troublesome due to the formation of precipitates and turbidity. The accuracy of this procedure is generally lower than with the internal standard, but still within 5%.

Prerequisites for the application of this procedure are:

a) a homogeneous sample
b) fairly similar concentrations in the sample and in the reference
c) the use of corrected intensities (where background values have been subtracted).

In the analysis of solid samples, it is difficult to obtain homogeneous samples: usually the sample is melted in borax or in lithium tetraborate. Tertian's procedure may be applied to solid samples using these fusion "pearls".

TABLE VII. SIMPLE DILUTION PROCEDURE USING SOLID SAMPLES

1) Extraction with solvents - drying
2) Grinding in a mill to 400 mesh
3) Dilution with cellulose 10-100 X
4) Preparation of pellet using a press
5) X-ray reading against reference pellet

TABLE VIII SYNTHETIC MIXTURE *

Element	% Actual	% Found	Notes
Ba	5,00	4,95	dil. 1 : 100 PE, L_α
Ca	5,00	4,97	» 1 : 100 PE, K_α
Br	5,00	4,94	» 1 : 10 LiF, K_α
P	1,55	1,51 (*)	» 1 : 100 PE, K_α
Zn	5,00	4,90	» 1 : 100 LiF, K_α
Pb	10,00	10,5	» 1 : 10 PE, M_α
Fe	5,00	5,11	» 1 : 10 PE, K_α
S	5,00	4,86	» 1 : 100 PE, K_α
Si	5,00	5,02	» 1 : 10 PE, K_α
Cl	5,00	5,20	» 1 : 10 PE, K_α
Cu	0,50	0,52	» 1 : 10 PE, K_α
Ni	0,50	0,46	» 1 : 10 PE, K_α

/303

(*) Calcium requires a correction

* Translator's note: Commas in numbers represent decimal points.

The fusion method is not completely satisfactory, both for the intrinsic difficulty of obtaining always homogeneous fusions (especially for silica), and for the complexity of the manual techniques.

We are investigating a different procedure for the preparation of analytical samples of solid materials using the dilution technique. Examples of these materials are deposits on valves, engines, filters, etc.

Table VII summarizes this procedure, which is simple and fast. The reference substances, however, have to be selected with care, because not all of them give good results: generally carbonates and oxides are preferred.

The results obtained with a synthetic mixture prepared in the laboratory are reported in Table VIII. Two preliminary dilutions of the sample in cellulose (1:10 and 1:100) had to be prepared. Analyses of real samples using this procedure are being carried out and compared with the results obtained from other analytical techniques, such as chemical, X-ray fluorescence, fusion, atomic absorption.

If this procedure will be found sufficiently accurate and precise, the fast analysis of complex solid mixtures will have progressed considerably.

Some elements with low atomic weight cannot be determined directly using X-rays or have a low sensitivity to this technique. For these cases, indirect determinations may be used; obviously the procedures become more complicated and take longer.

Table IX lists some indirect procedures.

TABLE IX. INDIRECT ANALYSES

Elements in the analyses	Compound	Elements determined
Boron	Barium borotartrate	Barium
Sodium	Sodium zinc uranyl acetate	Zinc/Uranium
Lithium	Lithium arsenate	Arsenic
Phosphorus	Berillium phosphate/ arsenate	Arsenic/Berillium
Phosphorus	Bismuth phosphate	Bismuth

TABLE X. INDIRECT PROCEDURE

Determination of silicon using the Si-Mo complex and X-ray fluorescence

Advantages:

Mo has an X-ray sensitivity that is 20 times higher.
Mo:Si ratio = 12

The final solution can be concentrated on a small surface.
The final readings are stable with time.

Sensitivity: 1 μg, equal to 0.1 ppm, using 10g of oil for the analysis.

TABLE XI. PROCEDURE

1) Mineralization of the sample.
2) Complexation in aqueous solution using ammonium molybdate.
3) Extraction of the Si-Mo complex with methylisobutyl ketone.
4) Addition of the Pb naphthenate internal standard evaporation on porous plate.
5) X-ray reading of the Mo L_α and Pb M_α analytical lines.

An indirect procedure for the determination of traces of silicon [2] has been developed to control the concentration of silicones in oils (5-20 ppm). /304

Table X details the advantages of this procedure. One should consider that silicon cannot be directly determined below 500 - 1000 ppm.

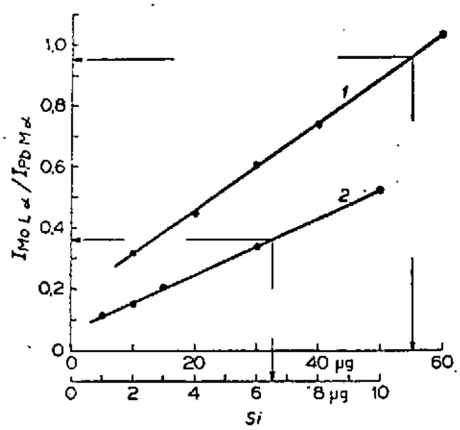

Figure 4. Calibration curve for the indirect determination of silicon using the silico-molybdic complex.

Table XI summarizes the procedure, while the calibration curves for this technique are depicted in Figure 4.

CONCLUSIONS

In conclusion, our experience with analytical procedures based on X-ray fluorescence spectrometry reveals that this technique offers many advantages:

1) Both solid and liquid samples can be analyzed. Liquid samples include liquids with some vapor pressure, such as gasolines; lead and sulfur content can be determined for these substances.

2) For many elements, concentrations of the order of parts per million can be determined.

3) This technique may be extended by indirect procedures to light elements which cannot be determined directly.

4) The rapidity, simplicity, and accuracy of this analytical procedure are higher than for chemical methods.

REFERENCES

1. Spectrochimica Acta, Vol. 24B, 1969, p. 447.

2. Being published on "Annali di Chimica".

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